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Mossbauer Effect Spectra of Ammonia Adsorption on a Supported Iron Catalyst

THE Mossbauer effect has been used to obtain structural information on ferric oxide supported on silica and on alumina[1-3]; the experimental conditions under which these studies were carried out did not, however, allow observations on chemisorption or reduction of the catalysts. This communication reports some initial work applying the Mossbauer effect to a study of supported iron catalysts which have been reduced with hydrogen.

A catalyst was prepared by impregnating silica gel with sufficient ferric nitrate solution enriched in iron-57 to produce a 3 weight per cent sample of iron on silica gel. After calcining in air at 500° C the catalyst was placed in a thin window glass cell and reduced by alternately adding hydrogen and outgassing at 450° C. A final outgassing

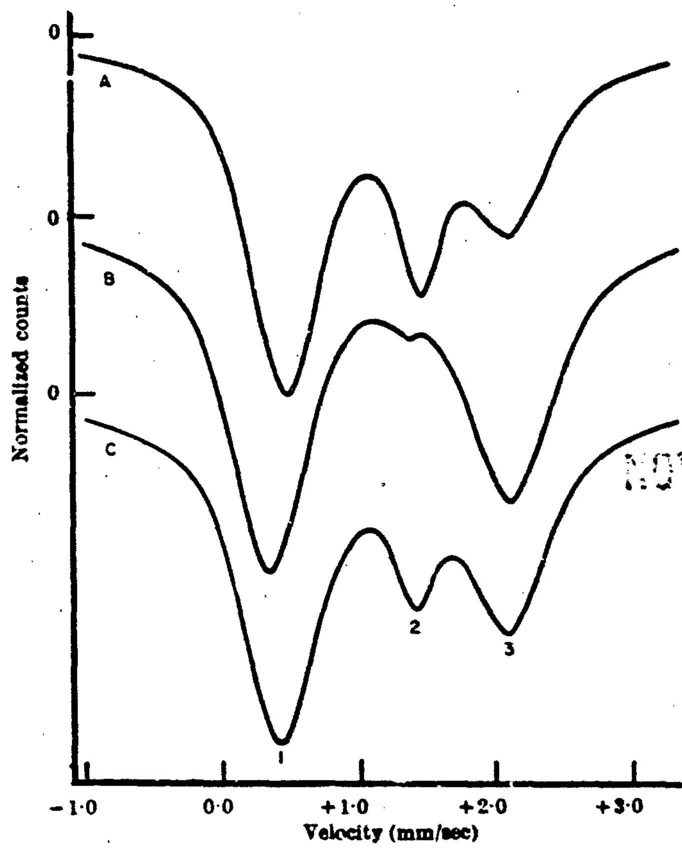

Fig. 1. Mossbauer effect spectra of the adsorption and desorption of ammonia on an iron-on-silica gel catalyst at 25° C.

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Table 1. DIFFERENTIAL CHEMICAL SHIFTS, δ_0, AND QUADRUPOLE SPLITTINGS ΔE_Q, FOR SPECTRA IN FIG. 1

Spectrum	δ_0 (mm/sec) 1–3	1–2	2	ΔE_Q (mm/sec) 1–3	1–2
A	+1·29	+0·96	+1·46	1·64	0·99
B	+1·23	+0·84	+1·34	1·75	1·00
C	+1·25	+0·91	+1·41	1·67	0·98

at 450° C attained a pressure of 8×10^{-7} torr. The Mossbauer effect spectrum of this preparation is shown as spectrum *A* in Fig. 1. The spectra in Fig. 1 are all normalized to a scale of zero to one between the baseline and the maximum of the largest peak, and represent a Lorentzian function fitted by computer to the experimental data. A constant acceleration spectrometer[4] was used with the source moving. A total of approximately 1,000,000 counts were obtained for each point, and the largest peak exhibits about a 7 per cent effect in each spectrum. On admitting ammonia to a total pressure of 1·35 torr, spectrum *B* in Fig. 1 was obtained. Prolonged pumping on the catalyst sample at room temperature did not change spectrum *B* appreciably. Outgassing at 100° C until a pressure of 1×10^{-6} torr was obtained did, however, result in a partial recovery of the initial spectrum as shown by spectrum *C* in Fig. 1. The original spectrum was obtained by outgassing again at 450° C. The values for the differential chemical shifts[5], that is, relative to sodium nitroprusside, and the quadrupole splittings are given in Table 1. The error is 0·01 mm/sec for all these results.

The spectrum of the reduced and outgassed catalyst must be representative of iron atoms in at least two different states on the surface. There appears to be no theoretical justification for a triplet in the absence of an applied magnetic field. Furthermore, the half-width at half-maximum is much smaller for the middle peak than for the other two. Numbered from left to right, peaks 1 and 3 appear to constitute a doublet caused by quadrupole splitting at one iron site. The values for the differential chemical shift, +1·29 mm/sec, and the quadrupole splitting, 1·64 mm/sec, are typical of a high-spin ferrous state. The middle peak presents a problem. It appears to be a singlet, but it is difficult to imagine an atom on, or just in the surface, as having a symmetrical electrical field gradient surrounding the nucleus. If an asymmetric electrical field gradient obtains at the nuclei of the iron atoms producing peak 2, then peak 2 is half a doublet with the other half superimposed on peak 1 or peak 3.

Kinetic studies on ammonia decomposition over iron catalysts indicate that dissociative chemisorption of ammonia takes place. If one assumes that ammine radicals are formed by chemisorption of ammonia on this catalyst, then peak 2 of spectrum *A* is probably produced by a high-spin ferric state. The ammine radical, with its strong tendency to donate electrons to the adsorption site, complexes with the $3d$ orbitals of the ferric ions and produces a high-spin ferrous complex on the surface, as indicated in spectrum *B*. The reversible nature of the surface complex is demonstrated by obtaining spectrum *C* on outgassing the sample.

In order for peak 2 to represent a ferric species it must be half a doublet with the other peak at the peak 1 position. The differential chemical shift for peak 2 alone is $+1.46$ mm/sec, a value much too large for a ferric ion. A doublet with one peak at position 1 and the other at 2 would have a differential chemical shift of $+0.96$ mm/sec, a value a little large but not unreasonable for a ferric ion. The probable state of the reduced iron on this supported iron catalyst is therefore a mixed ferrous–ferric oxide in the form of very small particles on the surface of the silica gel. The ferric ions must be on, or very near, the surface since they readily react to chemisorption of ammonia.

Further Mossbauer effect measurements are being made on supported iron catalysts as a function of catalyst preparation, support material, and chemisorption of various compounds in hopes of defining more precisely the nature of the active sites.

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13. ABSTRACT

A catalyst was prepared by impregnating silica gel with sufficient ferric nitrate solution enriched with Fe-57 to produce a 3% sample of iron on silica gel. The sample was calcined and then reduced with hydrogen at 450°C. The Mossbauer of this sample consisted of three peaks apparently produced by the superposition of two doublets having quadrupole splittings of 1.64 mm/sec for one and 0.99 mm/sec for the other. On adsorption of ammonia the middle peak almost vanishes, but the spectrum is recovered by outgassing at elevated temperatures. The results suggest that the sample is a mixed ferrous-ferric ocide on the surface of the silica gel and that on chemisorption the ammonia complexes into the d orbitals of the ferric ions.

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